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## SUMMARY

The effects of thermal exposure on the room temperature tensile strength and microstructure of a developmental 50  $\mu\text{m}$  CVD SiC fiber have been studied. The fibers were heat treated between 600 and 2000  $^{\circ}\text{C}$  in 0.1 MPa argon and air environments for up to 100 hr. In the as-fabricated condition, the fibers showed  $\sim 6$  GPa tensile strength. After argon treatment, the fibers showed strength degradation after 1 hr exposure beyond 1000  $^{\circ}\text{C}$ , but those exposed between 1600 and 2000  $^{\circ}\text{C}$  retained  $\sim 2$  GPa strength. TEM results showed microstructural changes both in the surface coating and SiC sheath. Flaws created by the rearrangement of carbon in the surface coating and growth of equiaxed SiC grain zone in the SiC sheath are the suggested mechanisms of strength degradation. After air treatment, fibers showed strength degradation after only 2 min exposure at 600  $^{\circ}\text{C}$ . Strength retention after 2 min at 1500  $^{\circ}\text{C}$  was  $\sim 2$  GPa. Oxidation of the surface coating is the primary reason for strength degradation.

## INTRODUCTION

SiC fibers fabricated by chemical vapor deposition methods (CVD) are being used as reinforcement for metal and ceramic matrix materials because of their chemical purity, high modulus, and high strength. SiC fibers, such as the well-known SCS-6 fibers from Textron Specialty Materials (TSM), Lowell, Massachusetts are themselves composites, consisting of a  $\sim 37$   $\mu\text{m}$  pyrolytic-carbon coated graphite core, a SiC sheath, and a carbon-rich surface coating as shown in figure 1(a). The SiC sheath has two zones: the outer zone is typically silicon-rich with high aspect ratio SiC grains with preferred radial orientation; the inner zone is typically carbon-rich with lower aspect ratio SiC grains (ref. 1).

It has been reported previously (refs. 2 and 3) that these fibers when heat treated in argon beyond 1500  $^{\circ}\text{C}$  showed recrystallization and growth of the outer silicon-rich zone of the fiber, but the inner carbon-rich zone of the fiber showed much retarded grain growth. In addition, a good correlation was found between the thickness of recrystallization zone and the tensile strength of the fibers. These studies suggested that CVD SiC fibers containing only the inner carbon-rich SiC zone microstructure should show better strength retention for high-temperature applications than those containing the silicon-rich SiC outer zone structure. Based on these observations, a 50  $\mu\text{m}$  CVD SiC fiber with carbon-rich SiC grains was developed by TSM. The objectives of this paper are to determine thermal exposure effects on strength and microstructure of this new fiber and to suggest possible strength degradation mechanisms.

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## EXPERIMENTAL

### Material

The 50  $\mu\text{m}$  SiC fiber used in this study was manufactured by CVD of SiC onto a heated pyrolytic carbon-coated  $\sim 25$   $\mu\text{m}$  graphite core in a single stage reactor. Microstructurally, this fiber and the standard grade of CVD SiC fibers (SCS-6) manufactured by TSM are distinctly different. Schematics of the fiber cross-sections are shown in figure 1. The 50  $\mu\text{m}$  SiC fiber contains a single zone of carbon-rich SiC, whereas the SCS-6 fiber contains two zones of SiC having different composition. The C/Si ratio in the SiC sheath of the 50  $\mu\text{m}$  SiC fiber is similar to that of the inner zone of the SCS-6 fiber as determined by electron microprobe. Both fibers had  $\sim 1$  to 3  $\mu\text{m}$  thick carbon-rich coating on the outer surface of the SiC sheath. The coating is used to improve strength and abrasion resistance of the fiber (ref. 4).

### Thermal Treatment and Tensile Testing

For heat-treatments, batches of fifteen individual fibers of length  $\sim 125$  mm were placed in grafoil envelopes. These envelopes were heated under an argon pressure of 0.1 MPa from 600 to 2000  $^{\circ}\text{C}$  for 1 to 100 hr in a graphite lined box furnace. For air exposure tests, individual fibers of length  $\sim 175$  mm were heated in a slot furnace for 2 min. Only 25 mm of the 175 mm length was heated to the maximum furnace temperature.

For room-temperature tensile testing, individual fiber specimens,  $\sim 60$  mm long, were placed at the center of a paper picture frame and the fiber ends were glued on to the picture frame using a fast curing epoxy leaving 25 mm as the gauge length. The picture frame was inserted in the pneumatic grips of a tensile testing machine and the sides of the picture frame were cut so that the fiber was freely supported between the grips. The fiber specimens were pulled at a constant cross-head speed of 1.3 mm/min. At least ten fibers were tested for each exposure condition.

### Transmission Electron Microscopy (TEM)

For transmission electron microscopy (TEM), fibers were placed in a mixture of epoxy and 6 mm alumina powder and packed longitudinally in a 3 mm diameter glass tube. After the mixture hardened,  $\sim 1$  mm thick disks were sectioned using a diamond saw. The disks were mechanically ground from both sides, dimpled, and ion-beam thinned. Details of specimen preparation technique are described elsewhere (ref. 3). The microscope used for conventional and analytical TEM was a Phillips 400T operating at 120 kV.

## RESULTS AND DISCUSSION

Effects of thermal exposure on the room-temperature tensile strength of the 50  $\mu\text{m}$  SiC fibers after heat treatment in 0.1 MPa argon for 1, 10, and 100 hr from 600 to 2000  $^{\circ}\text{C}$  are shown in figure 2. For comparison, the strength of the as-fabricated fibers ( $\sim 6$  GPa) is also shown in the figure. Each data point represents an average of 10 to 15 individual tensile tests and the error bar represents one standard deviation. After one hour heat treatment in argon up to 1000  $^{\circ}\text{C}$ , the fibers displayed strength levels similar to that of the as-fabricated fibers. From 1100 to 1600  $^{\circ}\text{C}$ , the tensile strength decreased with increasing temperature. In the same temperature range, a slight decrease in strength was noticed with increasing exposure time, but the temperature of exposure had a greater influence on strength degradation than the time of exposure. Beyond 1600  $^{\circ}\text{C}$ , the strength approached  $\sim 2$  GPa, and the time of exposure had no significant influence on the strength.

To identify flaws responsible for fiber fracture, attempts have been made to retain the primary fracture surface. Since fibers fractured into multiple pieces, identification of the primary fracture surface became difficult. Therefore, it is not clear whether the fractures are initiated by surface or interior flaws.

In figure 3, the average room-temperature tensile strength data for the 50  $\mu\text{m}$  SiC fibers after 1 and 100 hr exposure in argon between 600 and 2000  $^{\circ}\text{C}$  are compared with the data reported previously for the SCS-6 fibers in the same environment after 1 hr exposure in the same temperature range (ref. 2). Comparison of the best fit data in figure 3 indicates the following: First, the average as-fabricated tensile strength of the 50  $\mu\text{m}$  fibers is higher than

that of the SCS-6 fibers. Second, after 1 hr exposure the 50  $\mu\text{m}$  SiC fibers begin to show strength degradation at a lower temperature than the SCS-6 fibers. Third, the residual strengths of the 50  $\mu\text{m}$  SiC fibers after 1 hr exposure between 1400 and 1700°C are similar to those of the SCS-6 fibers. Fourth, the residual strengths of the 50  $\mu\text{m}$  SiC fibers exposed between 1600 and 2000 °C are generally higher than those of the SCS-6 fibers.

In figure 4, the room temperature tensile strength data of the 50  $\mu\text{m}$  SiC fiber after 1 hr exposure in argon between 600 and 1800 °C are compared with the data reported for the two types of SiC fibers derived from polymer precursor methods (Commercially available Hi-Nicalon and a developmental Hi-Nicalon) (ref. 5). For comparison purposes, the carbon to silicon (C/Si) ratios of the fibers are also given. The C/Si ratio of commercially available Hi-Nicalon is significantly higher than that of the 50  $\mu\text{m}$  SiC fibers. On the other hand, C/Si ratios of the developmental Hi-Nicalon and the 50  $\mu\text{m}$  SiC fibers are similar. According to figure 4, the 50  $\mu\text{m}$  SiC fiber shows strength degradation at a lower temperature (1000 °C) than both types of Hi-Nicalons. Beyond 1500 °C, the 50  $\mu\text{m}$  SiC fiber displays higher strength retention than both types of Hi-Nicalons. In fact, the developmental Hi-Nicalons have no strength at all after 1 hr exposure in argon beyond 1600 °C.

Influence of oxidation on the room-temperature tensile strength of the 50  $\mu\text{m}$  SiC fibers is shown in figure 5. For this study, fibers were heat treated in air for 2 min between 600 and 1500 °C and then tested at room temperature. Exposure temperatures above 1500 °C were not used to avoid strength degradation due to rapid and thick  $\text{SiO}_2$  growth on the fiber surface. Figure 5 shows that with increasing exposure temperature, strength of the fiber decreased continuously and for 2 min in air near 1000 °C attained a level similar to that of the fibers heat-treated between 1500 and 1800 °C for 1 hr in argon.

To determine argon heat-treatment effects on the microstructure of fibers, TEM analysis was performed on the as-received and heat-treated fibers. In all cases, microstructure of the pyrolytic carbon coated graphite core, SiC sheath, and surface coating were analyzed. Results of this analysis for the as-received fibers are shown in figure 6. The core of the fiber contains randomly oriented turbostratic carbon (TC) blocks (fig. 6(a)). The pyrolytic carbon layer on top of the graphite core consists of TC blocks having a textured orientation. This layer is  $\sim 0.6 \mu\text{m}$  thick (fig. 6(b)) and contains elongated SiC grains that are oriented normal to the radius of the fiber. The aspect ratio of these SiC grains is  $\sim 13$ . The carbon-rich SiC sheath is  $\sim 12 \mu\text{m}$  thick and consists of elongated  $\beta$ -SiC grains running along the radius of the fiber (fig. 6(c)). These  $\beta$ -SiC grains are highly faulted and have an aspect ratio of  $\sim 8$ . The surface coating on top of the SiC sheath has two layers (fig. 6(d)). The first layer adjacent to the carbon-rich SiC sheath consists of textured TC blocks and small elongated SiC grains similar to that present in the pyrolytic carbon layer on the core. The aspect ratio of SiC grains is  $\sim 8$ . The outer most carbon layer consists of textured TC blocks and finely dispersed SiC particulates.

One hour heat-treatment in argon at temperatures to 2000 °C had no significant effect on the microstructure of the graphite core and it remained turbostratic, but other zones of the fiber showed microstructural changes after 1 hr heat treatment beyond 1200 °C. With increasing temperature of exposure, spheroidization of SiC grains was observed in the pyrocarbon layer on top of the graphite core, and in the carbon-rich surface coating (figs. 7 and 8). At 1400 °C, a zone of equiaxed SiC grains formed at the interfaces of the SiC sheath and the pyrocarbon layer on the graphite core, and of the SiC sheath and the carbon-rich surface coating (figs. 7(a) and (b)). This zone, however, stopped growing after 1 hr exposure beyond 1600 °C. Typical thickness of the zone is  $\sim 100 \text{ nm}$ . As the heat treatment temperature was increased, no change in the aspect ratio of the faulted grains in the SiC sheath was noticed, but secondary SiC grains started nucleating and growing along the original grain boundaries and at the intersection of two or more grains (fig. 8). The rate of growth of these secondary grains was slow.

## DISCUSSION

It is evident from this study that the developmental 50  $\mu\text{m}$  SiC fibers show high as-received strength,  $\sim 6 \text{ GPa}$ , and that even after 1 hr argon treatment between 1600 and 2000 °C, these fibers display high retained strength,  $\sim 2 \text{ GPa}$ . This value is significantly higher than the strengths of SCS-6 or of Hi-Nicalon fibers after exposure to similar conditions. In argon environment, tensile strength degradation of the 50  $\mu\text{m}$  SiC fibers starts at  $\sim 1000 \text{ °C}$  and occurs in two stages as displayed by the shape of the tensile strength versus heat-treatment temperature plot (fig. 2): the first stage ranging from 1000 to 1200 °C and the second stage ranging from 1300 to 1600 °C.

The temperature at which strength degradation in the first stage starts also coincides with the deposition temperature of the carbon-rich surface coating (ref. 4). Based on earlier strength characterization studies of other high strength carbon-coated CVD SiC fibers (refs. 2 and 6), we believe that strength degradation in this fiber in the first



stage is due to changes occurring in the surface coating which exposes original surface flaws on the SiC sheath. Although in this temperature range, microstructural changes in the carbon-rich surface coating were not observed, except for a slight coarsening of SiC grains in the outer most carbon layer, circumstantial evidence indicates that rearrangement of carbon in the surface coating can occur. Such rearrangement could possibly lead to exposure of original flaws on the SiC sheath, thus nullifying the advantages of the carbon-rich coating. Strong evidence for this hypothesis comes from a previous study (ref. 7) which showed ~10 to 20 percent increase in the electrical conductivity after annealing the carbon-coated SiC fibers in argon beyond 1000 °C. This increase in electrical conductivity was possibly due to rearrangement of carbon in the surface coating. One of the factors responsible for the carbon rearrangement can be associated with diffusion of trapped by-products of CVD reaction in the surface coating. It has been documented that during deposition of CVD or PVD SiC, H<sub>2</sub> and Cl<sub>2</sub> are formed as by-products (ref. 8). Depending on the deposition conditions, significant amounts (3 to 15 at.%) of these by-products are generally trapped in the fibers. These by-products diffuse out when the fibers are heated above the deposition temperature, thus possibly causing rearrangement of carbon blocks and exposure of original flaws on the substrate.

The second stage of strength degradation takes place between 1300 and 1600 °C. In this temperature range, TEM study indicates that this degradation is the result of the flaws created by nucleation and growth of the equiaxed SiC grains in the SiC sheath at the pyrocarbon layer/C-rich SiC sheath, and the C-rich SiC sheath/C-rich surface coating interfaces, and along the grain boundaries of elongated SiC grains of the SiC sheath. The growth of the secondary SiC grains at the boundaries of the original grains is observed only in the 50 μm SiC fibers heat-treated beyond 1300 °C. Such growth was not observed in the heat-treated SiC fibers with Si-rich composition (SCS-6). The slow growth of these equiaxed SiC grains in the 50 μm SiC fibers with increasing time and temperature helps in limiting the size of the flaws. This allows the fiber to maintain the strength levels to ~2 GPa.

In air environment, strength loss in the 50 μm SiC fiber is seen even at 600 °C. This loss is attributed to oxidation of the carbon-coating, similar to the oxidation and strength loss seen in SCS-6 fiber exposed to air (ref. 6).

## SUMMARY OF RESULTS

(a) In comparison to other commercially available CVD or polymer derived SiC fibers, the 50 μm SiC fibers presently show the best room-temperature tensile strength in the as-fabricated condition and after exposure to high temperatures in argon .

(b) In argon environment, exposure of original surface flaws due to rearrangement of carbon-blocks in the coating, and the flaws created by the formation of equiaxed SiC grains are possibly some of the factors responsible for the strength degradation of the fibers.

(c) In air environment, flaws created during oxidation of the carbon-rich surface coating is the mechanism for strength degradation.

## CONCLUSIONS

Based on the characterization results, we conclude that the microstructures of the as-fabricated 50 μm SiC fiber are metastable and that microstructural changes occur after high temperature exposure. However, these changes stop after a certain time interval of exposure at ~1600 °C. Once the microstructure is stabilized, fibers still display high residual strength which may be controlled by the surface flaws.

Thus, CVD SiC fibers with slightly carbon-rich SiC composition appear to have better potential for high temperature composite applications than other CVD fibers with silicon-rich SiC compositions.

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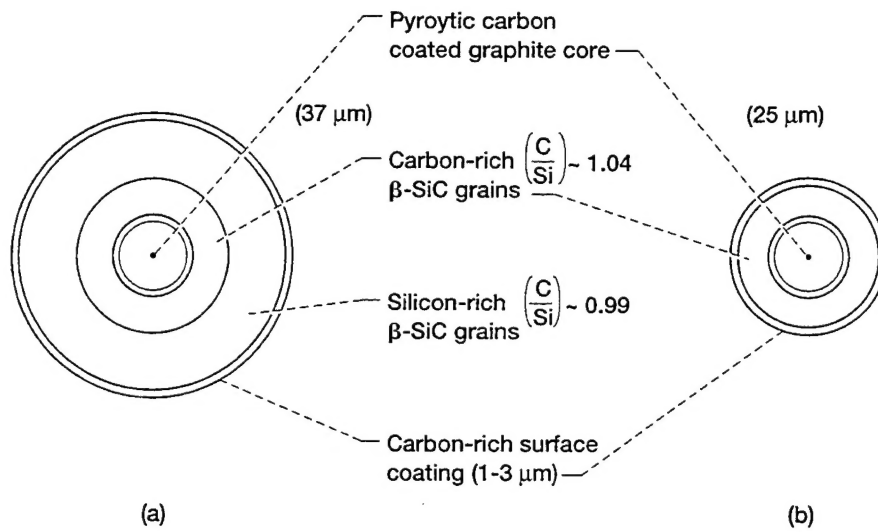


Figure 1.—Cross-section of CVD SiC fibers. (a) Textron SCS-6 fiber (~140 μm). (b) Textron developmental SiC fiber (~50 μm).

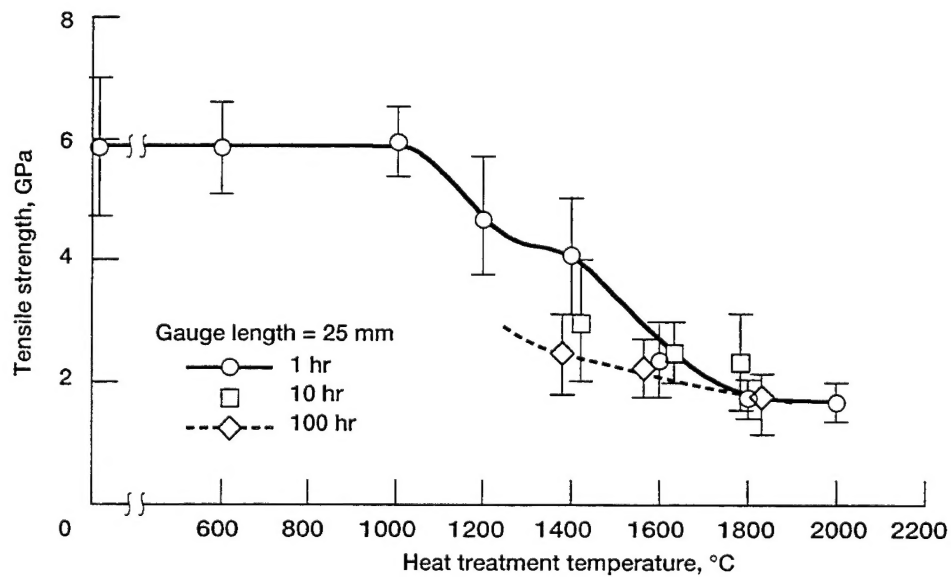


Figure 2.—Effects of temperature on the room-temperature tensile strength of 50 μm SiC fibers heat-treated in 0.1 MPa argon.

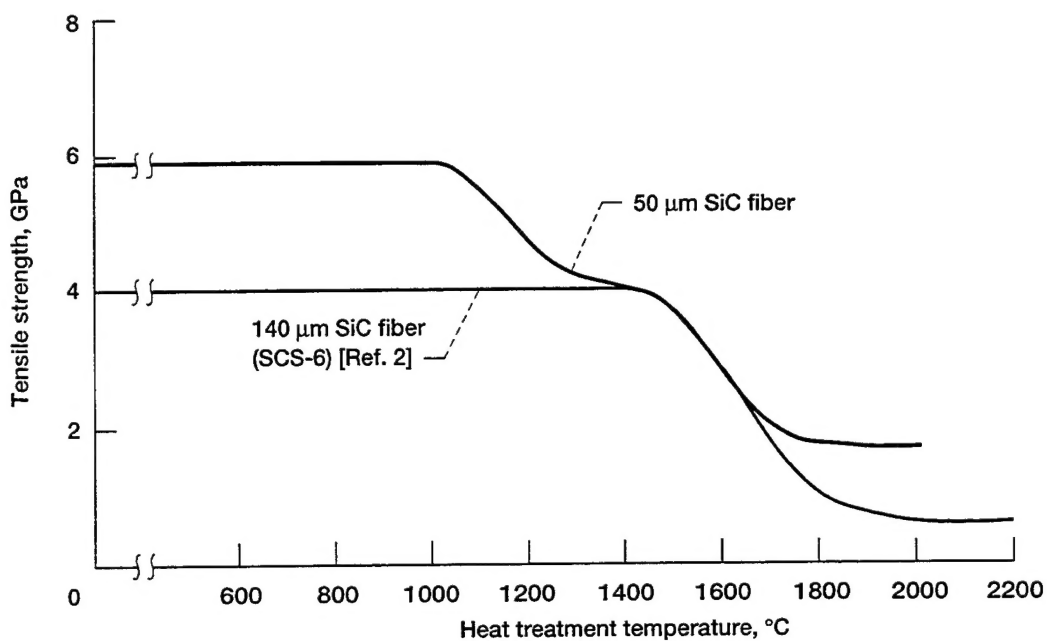


Figure 3.—Comparison of room-temperature tensile strengths of the 50  $\mu\text{m}$  and 140  $\mu\text{m}$  (SCS-6) SiC fibers after 1 hr heat-treatment in 0.1 MPa argon.

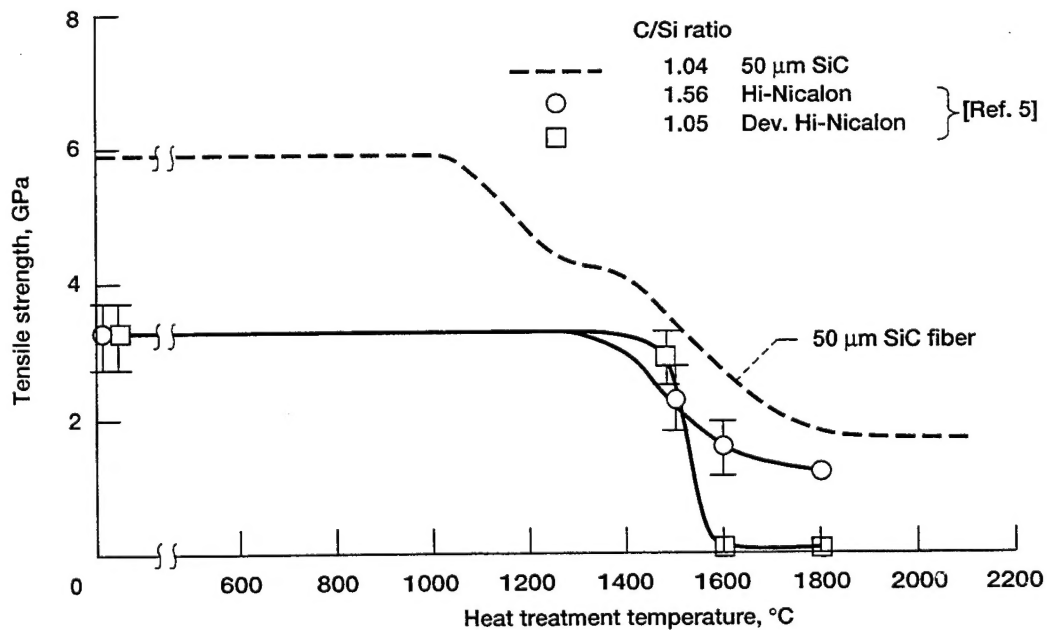


Figure 4.—Comparison of room-temperature tensile strengths of the 50  $\mu\text{m}$  and 14  $\mu\text{m}$  Hi-Nicalon SiC fibers after 1 hr heat-treatment in 0.1 MPa argon.

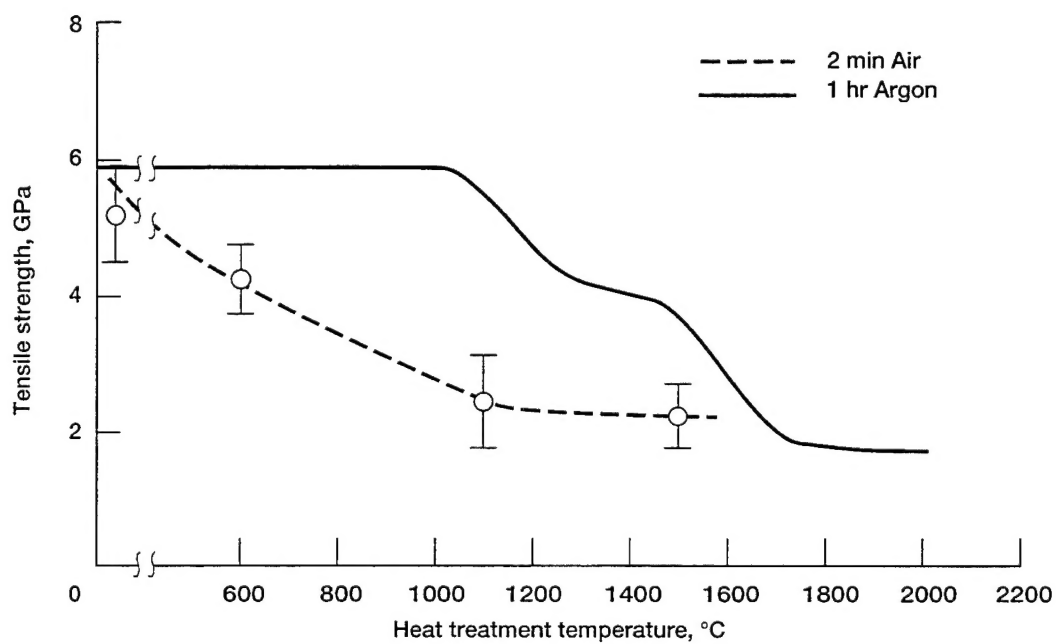


Figure 5.—Effects of temperature on the room-temperature tensile strength of the 50  $\mu\text{m}$  SiC fibers heat-treatment in air.

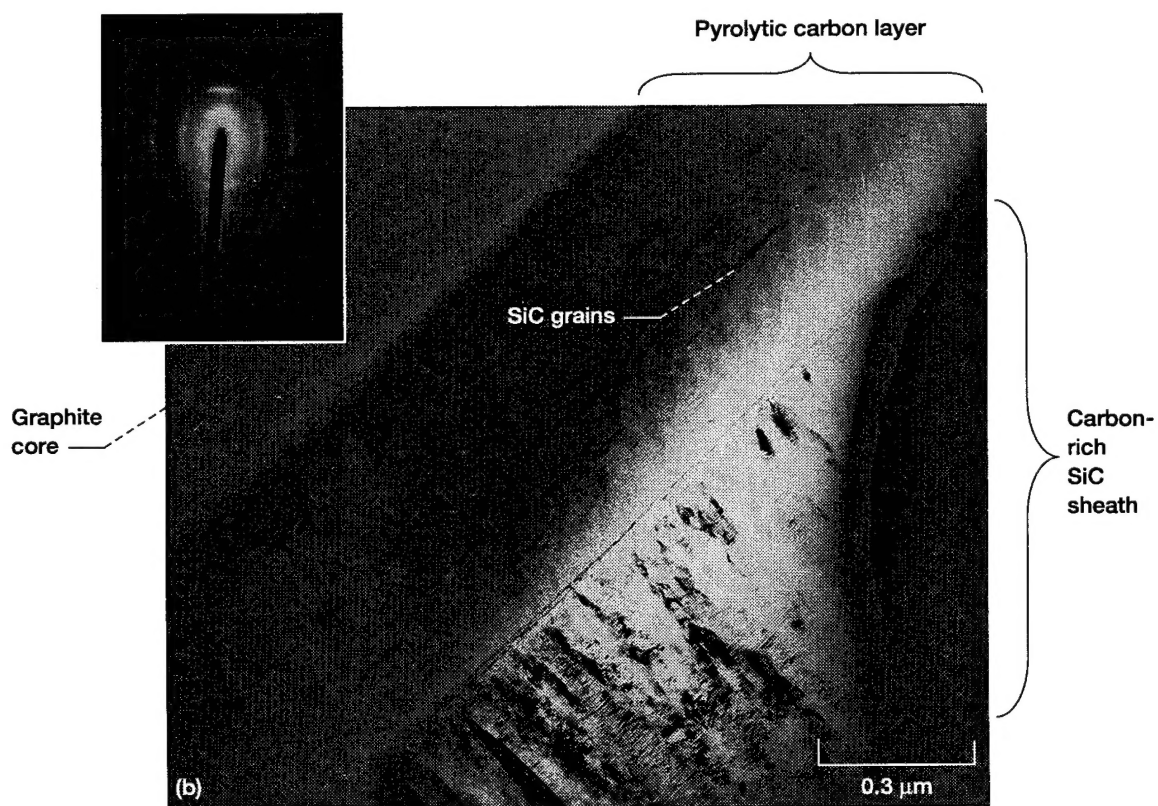
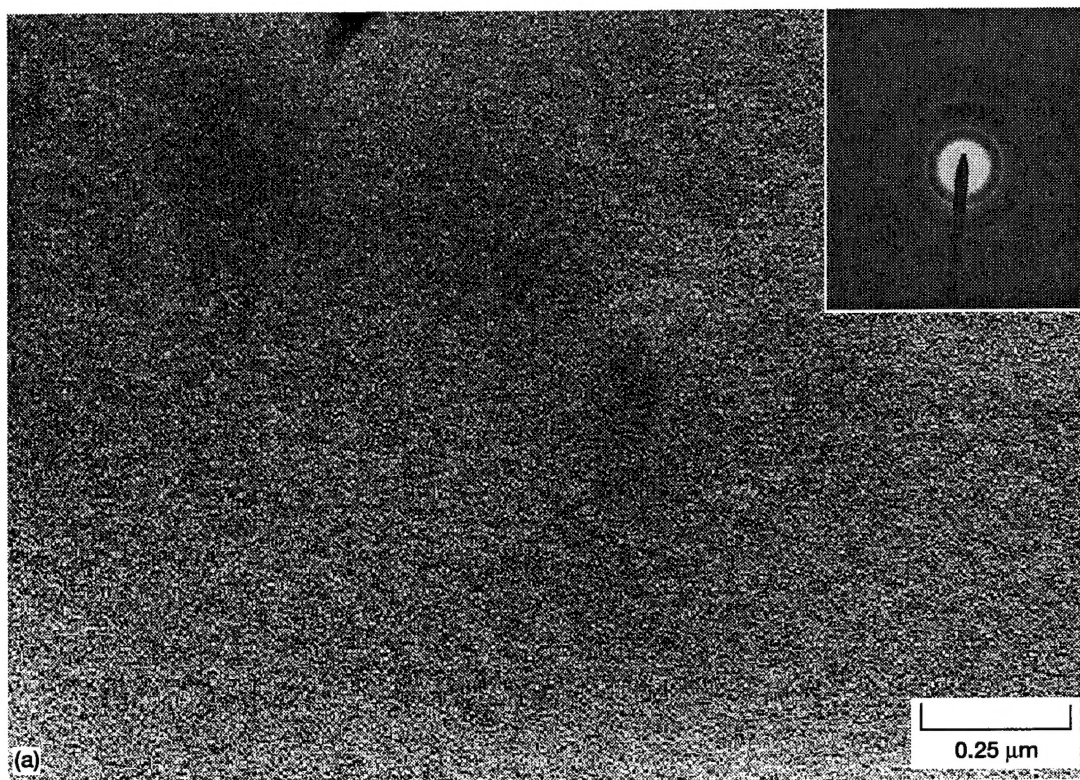


Figure 6.—TEM micrographs and corresponding SADP of different zones of an as-received 50 μm SiC fiber. (a) Graphite core. (b) Pyrolytic carbon layer on the carbon core. (c) Carbon-rich SiC sheath. (d) Carbon-rich surface coating.



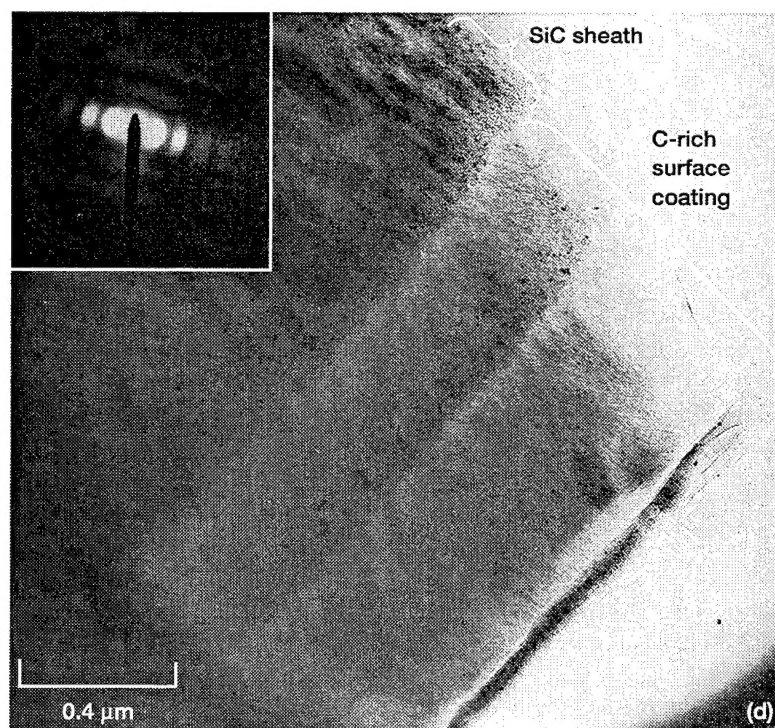
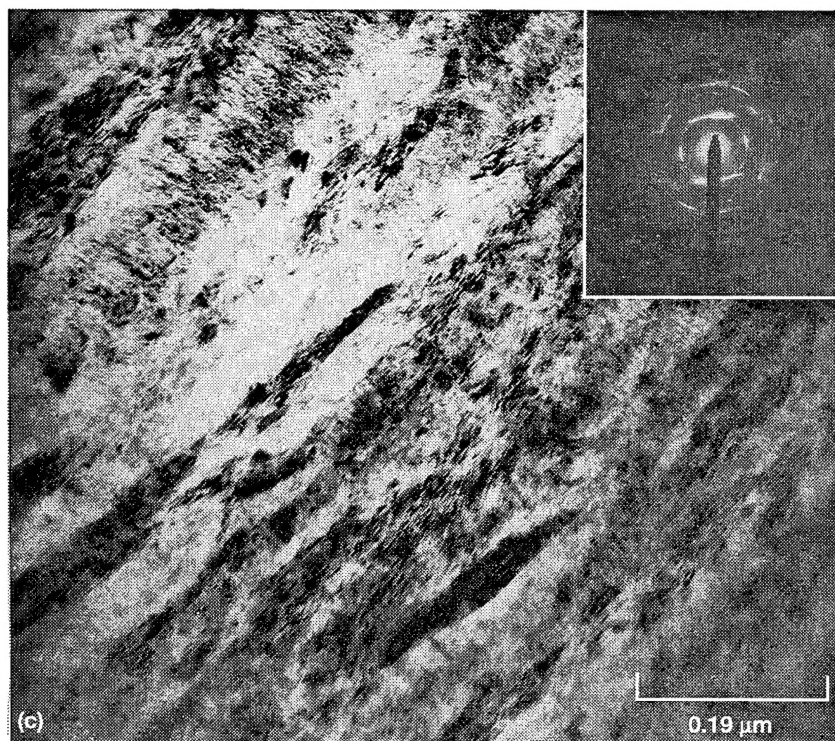


Figure 6.—Concluded. (c) Carbon-rich SiC sheath. (d) Carbon-rich surface coating.

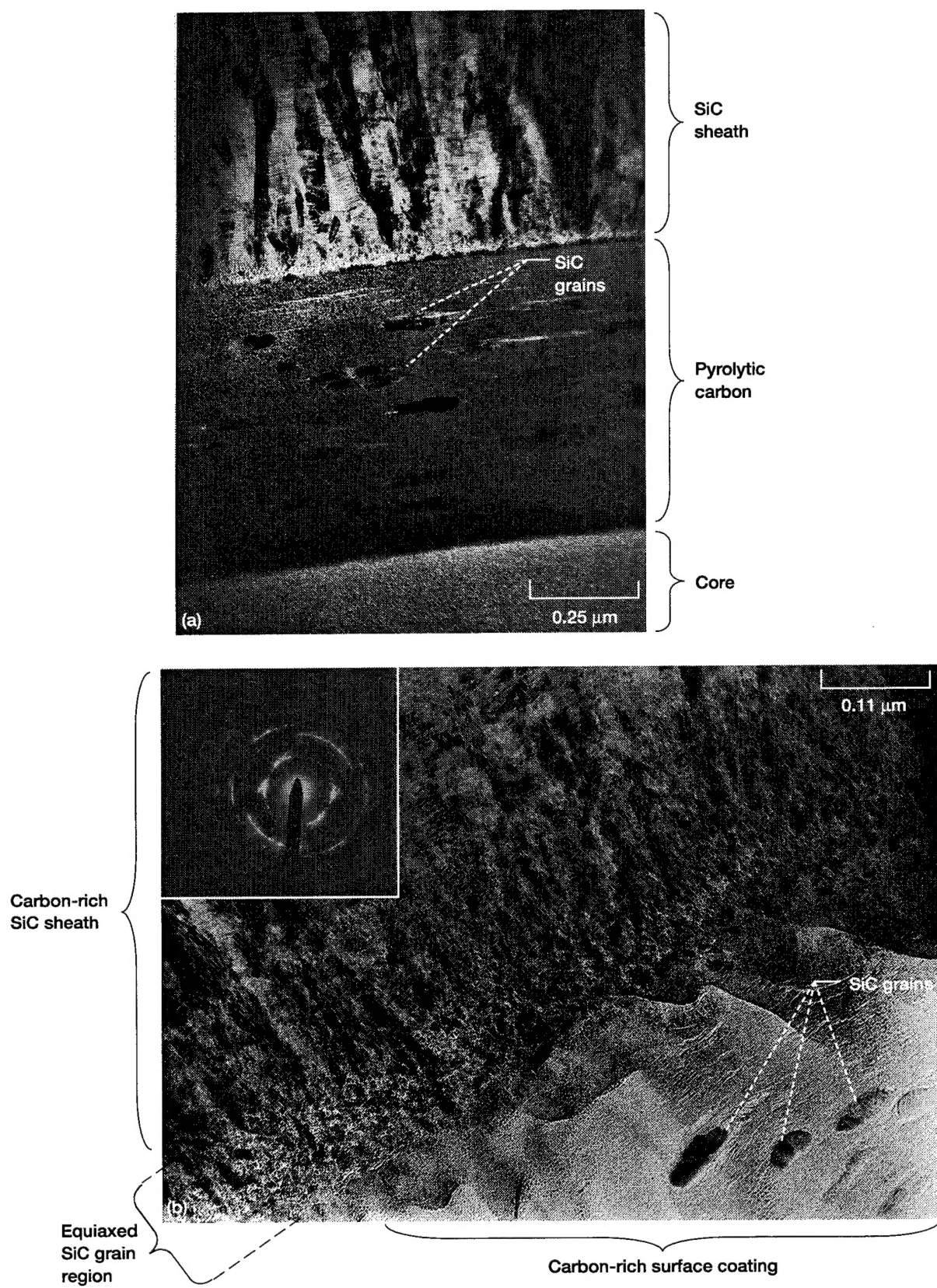


Figure 7.—TEM micrographs and corresponding SADP of a 50  $\mu\text{m}$  SiC fiber heat-treated in argon at 1400  $^{\circ}\text{C}$  for 1 hr. (a) Pyrocarbon layer on the graphite core. (b) SiC sheath and carbon-rich surface coating interface.

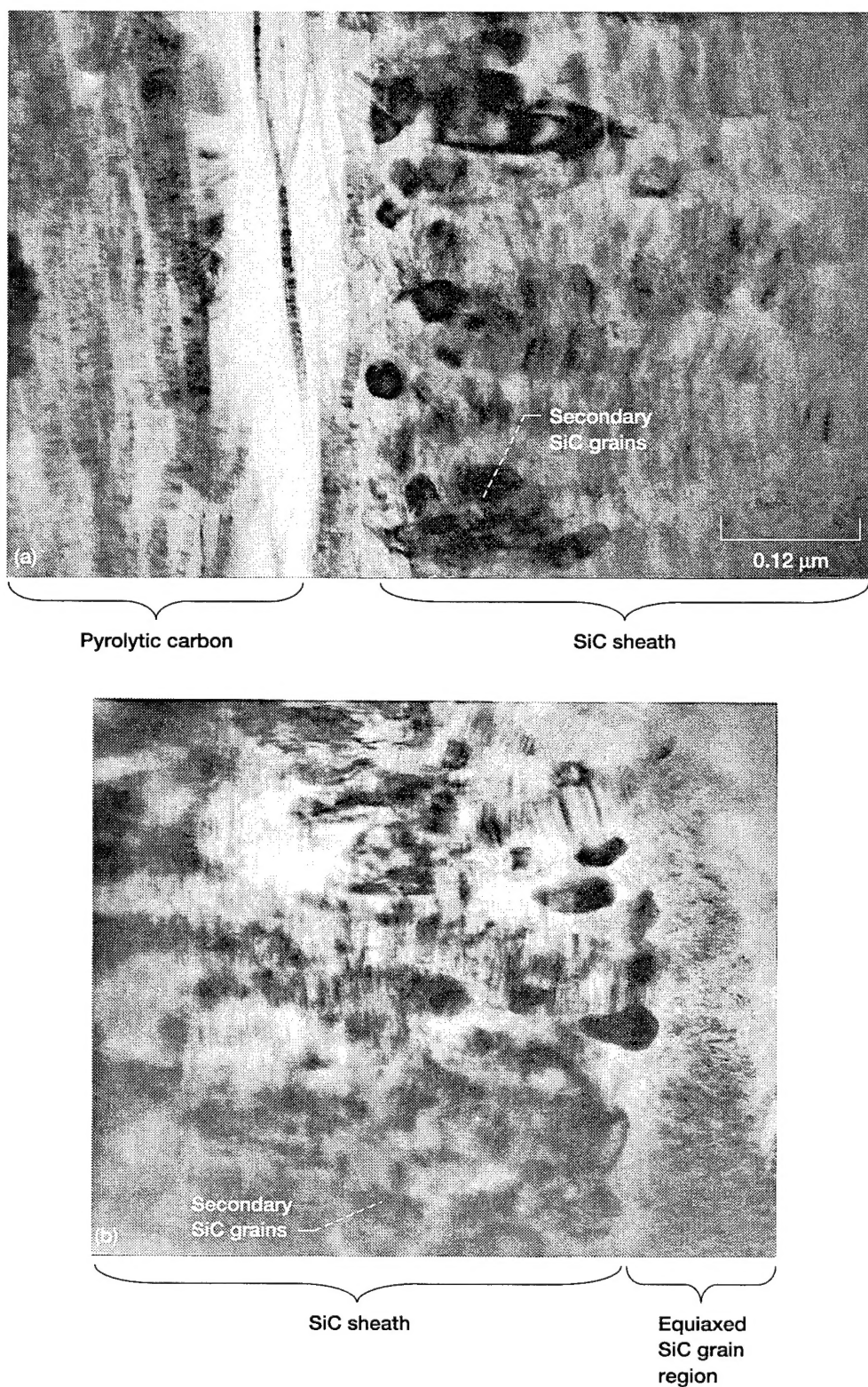


Figure 8.—TEM micrographs of the interfaces of a 50  $\mu\text{m}$  SiC fiber heat-treated in argon at 1800  $^{\circ}\text{C}$  for 1 hr. (a) Interface between pyrocarbon layer and SiC sheath. (b) Interface between SiC sheath and carbon-rich surface coating.



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